



Eur pâisches Patentamt  
Europæan Patent Offic  
Office européen des brevets



(11) Publication number:

**0 643 129 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 93202607.3

(51) Int. Cl.<sup>6</sup>: **C11D 17/06, C11D 11/00**

(22) Date of filing: 07.09.93

(23) Date of publication of application:  
15.03.95 Bulletin 95/11

(24) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IE IT LI LU NL  
PT SE**

(71) Applicant: **THE PROCTER & GAMBLE  
COMPANY  
One Procter & Gamble Plaza  
Cincinnati  
Ohio 45202 (US)**

(72) Inventor: **Wilkinson, Carole P. D.  
rue du Pévot 95  
B-1050 Ixelles (BE)**

(74) Representative: **Canonici, Jean-Jacques et al  
Procter & Gamble European Technical  
Center N.V.  
Temselaan 100  
B-1853 Strombeek-Bever (BE)**

(54) **Process for preparing detergent compositions.**

(57) A granular detergent composition or component having a bulk density of at least 650g/l is prepared by mixing a hydratable compound, e.g. anhydrous sodium carbonate, with a spray-dried powder, preferably in a high-speed mixer, and also adding water to the spray-dried powder, preferably in an agglomeration step carried out in a moderate-speed mixer downstream of the high-speed mixer. The agglomeration step may be carried out in the presence of a nonionic surfactant. After the agglomeration step, the resultant granular material may be aged in a fluidised bed apparatus. The product has improved dispensing and solubility properties.

EP 0 643 129 A1

Field of the Invention

5 The present invention relates to a process for preparing a granular detergent composition or a component of a granular detergent composition, in particular such a composition or component having a high bulk density.

Background of the Invention

10 Conventionally, granular detergent compositions have been manufactured by spray-drying processes. In such processes, one or more detergent components, such as surfactants and builders, are mixed with water and the resultant slurry is heated and spray-dried in a tower. Such processes are described, for example, by A. Davidsohn, "Spray Drying and Dry Neutralisation of Powdered Detergents", *J. Am. Oil Chemists' Soc.*, Vol. 55, January 1978, pp. 134-140. Although the spray-dried granules so obtained may exhibit a good solubility, the product tends to have a low bulk density, and hence the packing volume is large.

15 There has been a recent trend in the detergents industry towards the manufacture of so-called concentrated or "compact" detergent powders, which typically have bulk densities of 600-650 g/l or higher. Although various processes for the production of detergent granules which do not require a spray-drying stage have been described in the literature, there is still a need for processes whereby products of high bulk density may be prepared by a spray-drying route. However, the scope for increasing the bulk density 20 of the detergent product by adjusting the composition of the slurry fed to the spray-drying tower is limited and efforts have therefore been directed towards processes for the densification of spray-dried powders, i.e. the powders obtained from the spray-drying tower.

25 One process for the post-tower densification of spray-dried powders is described in EP-A-0,367,339 (Unilever) and its equivalent US-A-5,133,924, which process comprises treating a spray-dried powder in a high-speed mixer/densifier, the mean residence time being from 5 to 30 seconds, the so-treated material then being treated in a moderate-speed granulator/densifier with a mean residence time of from 1 to 10 minutes, whereby the material is brought into, or maintained in, a deformable state (the powder being considered to be in a deformable state if its compression modulus is less than 25 MPa). The material obtained from the moderate-speed granulator/densifier is then subjected to drying and/or cooling so that it 30 is no longer in a deformable state and is ready for use, handling and storage. However, this process may give rise to a product that contains a substantial quantity of fine particles (average size 350 µm) which, in turn, can cause poor dispensing of the product in automatic washing machines and also an undesirable level of gelling during usage. Moreover, the particles in the product may be soft and may cake easily in storage or under compression.

35 Disadvantages of the said process have also been disclosed in EP-A-0,390,251, which suggests that the process may be improved by adding 0.1 to 40% by weight of a powder, e.g. a fine zeolite powder, to the material in the moderate-speed granulator/densifier or to the material between that machine and the high-speed mixer/densifier. However, the addition of the zeolite may retard or prematurely inhibit the agglomeration process leading to poor granule formation.

40 Summary of the Invention

The present invention provides a process for preparing a granular detergent composition or component having a bulk density of at least 650g/l, which process comprises treating a spray-dried material (which 45 term includes herein spray-dried powder, granules or like particulate material) in a mixer, characterised in that water is added to and/or included in the spray-dried material, and in that the spray-dried material is treated in the said mixer in the presence of a hydratable compound and optionally of water.

The expression "in the presence of a hydratable compound and optionally of water" refers not only to a hydratable compound and water as such but also to a hydratable compound and/or water that have/has 50 undergone at least partial reaction. Addition of further hydratable compound and/or of water downstream of the said mixer is not precluded.

Description of Exemplary Embodiments

55 The spray-dried material will comprise one or more ingredients suitable for use in or as a detergent composition; preferably, it will contain at least one surfactant and/or at least one builder.

Suitable surfactants may be selected from anionic, nonionic, amphoteric, zwitterionic and cationic surfactants and mixtures of two or more of such surfactants. Preferred spray-dried materials include those

which contain at least one anionic surfactant, optionally in admixture with at least one nonionic surfactant.

Anionic surfactants include the water-soluble salts of higher (e.g. C<sub>8</sub>-C<sub>24</sub>) fatty acids; the water-soluble alkyl sulfates, especially those obtained by sulfating the higher (e.g. C<sub>8</sub>-C<sub>18</sub>) alcohols, such as those produced by reducing the glycerides of tallow or coconut oil; the water-soluble alkyl benzene sulfonates, especially those in which the alkyl group, which may have a straight or branched-chain configuration, has 9 to 20, preferably 9 to 15, carbon atoms; the water-soluble alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; the water-soluble fatty acid monoglyceride sulfonates and sulfates; the water-soluble alkyl phenol ethylene oxide ether sulfates containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 12 carbon atoms; the water-soluble alkyl ethylene oxide ether sulfates containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains 10 to 20 carbon atoms; the water-soluble salts of esters or alpha-sulfonated fatty acids containing 6 to 20 carbon atoms in the fatty acid group and 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing 2 to 9 carbon atoms in the acyl group and 9 to 23 carbon atoms in the alkane moiety; water-soluble alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and 1 to 30 moles of ethylene oxide; water-soluble olefin sulfonates containing from 12 to 24 carbon atoms; and betaalkyloxy alkane sulfonates containing 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety. Where appropriate, the term "alkyl" in the preceding list may include the alkyl portion of an acyl group. The water-soluble species may contain an alkali metal, ammonium, alkylammonium or alkylammonium counterion; the potassium and, more especially, the sodium salts are preferred.

Preferred anionic surfactants include the linear or branched-chain alkyl benzene sulfonates wherein the alkyl group has 10 to 16 carbon atoms, especially linear straight-chain alkyl benzene sulfonates in which the average number of carbon atoms in the alkyl group is from 11 to 13 (commonly abbreviated to C<sub>11</sub>-C<sub>13</sub> LAS); alkyl sulfates having 10 to 18 carbon atoms in the alkyl group; and mixtures thereof.

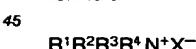
Nonionic surfactants include the condensation products of alkyl phenols, especially those having a straight or branched-chain configuration and containing 6 to 16 carbon atoms, with alkylene oxide, especially with 4 to 25 moles of ethylene oxide per mole of alkyl phenol; the water-soluble condensation products of aliphatic alcohols, especially those containing 8 to 22 carbon atoms in a straight-chain or branched configuration (especially as an alkyl group containing 9 to 15 carbon atoms), with alkylene oxide, especially with 4 to 25 moles of ethylene oxide per mole of alcohol; and the condensation products of propylene glycol with ethylene oxide. Other nonionic surfactants include the alkyl polyglucosides.

Semi-polar nonionic surfactants include water-soluble amine oxides and phosphine oxides containing, in either case, one alkyl group of 10 to 18 carbon atoms and two groups selected from C<sub>1</sub>-C<sub>3</sub> alkyl and C<sub>1</sub>-C<sub>3</sub> hydroxyalkyl groups; and water-soluble sulfoxides containing one alkyl group of 10 to 18 carbon atoms and a C<sub>1</sub>-C<sub>3</sub> alkyl or C<sub>1</sub>-C<sub>3</sub> hydroxyalkyl group.

Ampholytic surfactants include derivatives of aliphatic secondary and tertiary amines and aliphatic derivatives of heterocyclic secondary and tertiary amines, in which in each case the aliphatic moiety can be either straight or branched-chain and in which one of the aliphatic substituents contains 8 to 18 carbon atoms, at least one aliphatic substituent containing an anionic water-solubilising group, e.g. carboxy, sulfonate or sulfate.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, quaternary phosphonium and tertiary sulfonium compounds in which one of the aliphatic substituents contains 8 to 18 carbon atoms.

Useful cationic surfactants include water-soluble quaternary ammonium compounds of the general formula



wherein R<sup>1</sup> is alkyl having 10 to 20, preferably 12 to 18, carbon atoms and R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently an alkyl with 1 to 7 carbon atoms, preferably methyl; and X<sup>-</sup> is an anion, typically a halide and preferably chloride. Examples of such compounds include C<sub>12</sub>-C<sub>14</sub> alkyl trimethylammonium chloride and cocoalkyl trimethylammonium methosulfate.

The spray-dried material may contain a detergent builder to assist in the control of mineral hardness, whether by precipitation, sequestration or ion exchange. Suitable builders may be selected from various water-soluble, alkali metal, ammonium or substituted (alkyl or alkylol) ammonium phosphates, poly-phosphates (including tripolyphosphates, pyrophosphates and glassy polymeric metaphosphates), phosphonates, polyphosphonates, carbonates (including bicarbonates and sesquicarbonates), silicates, borates and polyhydroxysulfonates. The alkali metal, especially sodium, salts of these are preferred. Organic builders also come into consideration, such as polycarboxylates, for example citric acid and water-

soluble salts thereof, succinates, oxydisuccinates, imidodisuccinates, ethylene diamine tetramethylene phosphonic acid or ethylene diamine tetraacetic acid.

A preferred class of builders comprises aluminosilicate ion-exchange materials. These may be crystalline or amorphous in structure and can be naturally occurring or synthetically derived. Suitable 5 aluminosilicates are commercially available. Preferred synthetic crystalline aluminosilicate ion-exchange materials include the zeolites, e.g. zeolite A, zeolite P and zeolite X.

A further, optional component of the spray-dried materials may be selected from various organic polymers, some of which may also function as builders to improve detergency. Such polymers include sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl 10 celluloses, for example sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols, polyacrylamides, polyacrylates and various copolymers such as those of maleic and acrylic acids.

Polymeric polycarboxylate builders include the water-soluble salts of homopolymers and copolymers of 15 aliphatic carboxylic acids such as maleic, itaconic, mesaconic, fumaric, aconitic, citraconic and methylenemalic acids.

The spray-dried material may optionally contain one or more neutral or alkaline organic or inorganic salts which have a pH in solution of 7 or higher. These assist in providing the desired density and bulk to 20 the detergent granules and, although some of the salts are inert, many may also function as a detergency builder in the laundering solution. Such salts include the alkali metal, ammonium or substituted (alkyl or alkylol) ammonium chlorides, fluorides and sulfates, for example sodium sulfate.

Other ingredients commonly used in detergent compositions include flow aids, colour speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil-suspending agents, soil-release agents, dyes, dye-transfer-inhibiting polymers (e.g. PVP), softening agents (e.g. kaolin particles as dry mixes), fillers, optical brighteners, germicides, pH-adjusting 25 agents, nonbuilder alkalinity sources, hydrotropes, enzymes, enzyme-stabilising agents, chelating agents and perfumes. Numerous examples of such components as well as further examples of surfactants and builders will be found in the literature, for example International Patent Application WO92/22629, the teachings in which and in the references mentioned therein are incorporated herein by reference.

Desired ingredients that are not included in the spray-dried material (for example those which cannot be 30 spray-dried on account of their heat sensitivity) may be added to the spray-dried material at any suitable stage after the spray tower; thus, for example, they may be added during the course of the process of this invention or they may be added to and mixed with, by methods known in the art, the densified granules obtained by the process of the present invention in order to obtain a finished product. It will be appreciated, however, that, depending upon their composition, the densified granules obtained by the present process 35 may themselves constitute a serviceable detergent composition.

In accordance with the present invention, a hydratable compound is added to the spray-dried material. Preferred hydratable compounds are compounds, for example anhydrous compounds, capable of binding 40 water, upon contact therewith at temperatures encountered in the process, in the molecule, in a crystal or in a clathrate or the like, but especially as water of crystallisation, to form a stable hydrate. Although such hydratable compounds as citric acid come into consideration, it is preferred to use a hydratable salt, e.g. an alkali metal carbonate, bicarbonate, (poly)phosphate, citrate or sulfate. The most preferred hydratable salt is sodium carbonate. A commercial grade of anhydrous sodium carbonate is available as "soda ash". Other hydratable salts include sodium sulfate or, more preferably, sodium citrate (anhydrous), sodium bicarbonate or sodium tripolyphosphate. Mixtures of two or more hydratable compounds may also be used. The 45 hydratable compound will generally have a fine particle size, the average particle size being usually from 0.1 to 250 µm, preferably from 1 to 100 µm. In principle, there is no upper limit on the amount of hydratable compound but it will usually be added in an amount of up to 35%, e.g. up to 30%, by weight of the dry matter in the spray-dried material. Normally, the amount of hydratable salt will be at least 5% by weight of the dry matter in the spray-dried material. Although the applicant does not wish to be bound by 50 any hypothesis, it is believed that the hydratable compound provides hard seed particles that encourage particle growth in the spray-dried material by agglomeration. In contrast, any carbonate in the spray-dried material as obtained from the spray tower is not available for seeding and, because generally hydrated, for structuring the material.

In accordance with the present invention, water is also added to and/or included in the spray-dried 55 material. The moisture content of spray-dried material as obtained from the tower is usually insufficient to achieve satisfactory results; accordingly, the present process is usually practised by adding water to the spray-dried material. Various orders of addition are possible: however, although the water may be added before, during and/or after the addition of the hydratable compound, it is preferred to add the water after the

hydratable compound has been added to the spray-dried material more preferably after the hydratable compound and spray-dried material have been thoroughly or intimately mixed together. Portionwise addition of the water at different stages of the present process is also possible. Also, it is to be noted that the water need not be supplied as such (e.g. as mains or tap water) but can be the aqueous component of a solution.

- 5 dispersion, paste or other mixture, e.g. a silicate solution, a polymer solution or a surfactant paste. Normally, the amount of water in the system (i.e. the total of any water present in the spray-dried material as supplied to the present process and the water (if any) added to the spray-dried material during the present process) will be up to 30% by weight relative to the dry matter in the spray-dried material, e.g. up to 25%, preferably 10 to 25% and more preferably 10 to 20%. Typically, the amount of water added will be
- 10 from 0 to 20%, e.g. 0 to 15%, and preferably from 2 to 15%, by weight of the dry matter in the spray-dried material.

The process of this invention may be carried out in a continuous or batchwise manner. In currently preferred embodiments of the invention, the spray-dried material is processed in a first mixer, which is generally a high-speed or moderate-speed mixer, preferably a high-speed mixer (which term herein includes a high-shear mixer), in which the spray-dried material will usually be ground and/or densified, and is subjected to further processing downstream of the first mixer, generally in order to promote agglomeration (which term includes granulation and the like) and, possibly, (further) densification. In these preferred embodiments, the material is conveyed from the first mixer into a second mixer in which the material generally undergoes agglomeration (or further agglomeration), thereby increasing the particle size and reducing or eliminating the content of fines. Although a rotating-drum apparatus comes into consideration, the second mixer is generally a high-speed or moderate-speed mixer, preferably a moderate-speed mixer (which term herein includes a moderate-shear mixer).

It may be mentioned here that the description of an apparatus herein as a "mixer" does not necessarily imply that an admixture is made to or blended with the spray-dried material in that apparatus; a "mixer" 25 may possibly serve, in certain embodiments, just to agitate the material therein and effect, for example, particle-size reduction and/or densification or, as the case may be, particle-size increase, agglomeration, granulation and/or densification.

If the first mixer is coupled directly to the spray-drying process, "wet" spray-dried material, i.e. still containing a significant level of moisture, may be used; this reduces the drying load in the spray-drying tower, thereby increasing capacity. However, the material leaving the tower may alternatively be passed through one or more preliminary stages before entry into the first mixer.

A typical high-speed mixer will generally comprise a mixing chamber having a shaft mounted therein for rotation about its longitudinal axis, said shaft having a plurality of mixing elements (knives, blades, paddles or the like) mounted thereon. The speed of rotation of the shaft may be generally from 100 to 2500, 35 preferably 600 to 2000, rpm (revolutions per minute). In addition to the shaft-mounted mixing elements, the mixer may also have separately mounted cutting or chopping devices. The residence time of the material in the high-speed mixer will depend upon a number of factors, including the rotational speed of the shaft, the position and the number of the mixing elements, the efficiency of the mixing elements at impelling the material through the mixer and the size of the outlet opening (which will normally be adjustable by means of a weir). In mixers, such as the Schugi (trade mark) granulator, in which the material falls vertically downwards through the machine, the residence time can be as low as one second; normally, the residence time in the high-speed mixer will not exceed one minute. The residence time of the material within a high-speed machine is typically from 5 to 30 seconds. (Residence times herein are, of course, "mean" residence times.)

45 Currently preferred are high-speed mixers from the Lödige (trade mark) CB range, e.g. the CB55, the CB40 or the CB30 recycler. In these, the mixing chamber is formed by a static hollow cylinder arranged with its axis horizontal or substantially horizontal and having a rotatable shaft mounted along its longitudinal axis. Other mixers also come into consideration, for example a Drais (trade mark) K-TTP80 mixer or a Littleford (trade mark) mixer, as do batch mixers, such as Eirich (trade mark) mixers operated at high speed.

50 A typical moderate-speed mixer will generally comprise a mixing chamber in which is mounted a rotatable shaft, on which shaft are mounted a plurality of mixing elements (knives, blades, paddles or the like). The speed of rotation of the shaft may generally be from 40 to 160, preferably from 60 to 150, rpm. In addition to the shaft-mounted mixing elements, the mixer may also comprise separately mounted cutting or chopping devices, which may be used to control the agglomeration process, for example to inhibit over-agglomeration. The residence time of the material in a moderate-speed mixer will depend upon a number of factors, including the rotational speed of the shaft, the position and the number of the mixing elements, the efficiency of the mixing elements at impelling the material through the mixer and the size of the outlet opening (which will normally be adjustable by means of a weir). Normally, the residence time will be from 1

to 10 minutes, preferably from 2 to 5 minutes.

Currently preferred are moderate-speed mixers from the Lödige (trade mark) KM range, also known as Lödige Ploughshare mixers, e.g. the KM 300, KM600, KM 3000 or KM 4200. In these, the mixing chamber is formed by a static hollow cylinder arranged with its axis horizontal or substantially horizontal and having a rotatable shaft mounted along its longitudinal axis, at least a proportion of the mixing elements that are mounted on the shaft usually having a generally ploughshare configuration. Other mixers also come into consideration, e.g. the Drais (trade mark) K-T 160. Moderate-speed mixers suitable for batch processing include Lödige FM mixers, Patterson Kelly (trade name) V blenders and Eirich mixers operated at lower speeds.

10 The material may be treated in the first mixer at any suitable temperature, e.g. from 15°C to 50°C, more usually 20°C to 40°C, e.g. 25°C to 30°C. The material may be treated in the second mixer at any suitable temperature, e.g. from 25°C to 80°C, more usually 35°C to 60°C.

In certain preferred embodiments, the hydratable compound and the spray-dried material are thoroughly or intimately mixed together in the first mixer. In such embodiments, for instance, the hydratable compound may be added to the spray-dried material prior to entry into the first mixer or the spray-dried material and hydratable compound may be fed separately into the first mixer, for example through respective inlets in the mixer; when the process is carried out in a batchwise manner, it would, of course, be conceivable to add the spray-dried material and the hydratable compound sequentially through the same inlet. In such embodiments, the water may, for example, be added in either or both of the first mixer and

20 the second mixer; preferably, the water is added to the mixture in the second mixer.

One or more additional substances may be added to the spray-dried material and/or the hydratable compound before or during the mixing thereof. For example, a nonionic surfactant may be added, typically in an amount of up to 15%, preferably up to 12%, e.g. 0.1-10%, by weight of the dry matter in the spray-dried material, as a binder in order to promote good agglomeration. It is, of course, also possible to include 25 a nonionic surfactant in the spray-dried material itself or to add nonionic surfactant downstream of the first mixer, e.g. in the second mixer or by spraying it on during the admixing of the final ingredients to obtain the finished product.

In the present process, the addition of the water may be effected by spraying the water onto the spray-dried material or the mixture thereof with the hydratable compound, as the case may be; thus, the water 30 may be sprayed through one or more (atomizing) spray-heads or nozzles, the resultant (fine) droplets of water being incorporated efficiently and thoroughly into particulate mass. Of course, the water can be added by other means; for example, it may be added via a pipe provided that it is adequately dispersed, e.g. by the blades or other elements of a mixing, cutting or chopping device. Although the applicant does not wish to be bound by any hypothesis, it is believed that the water will hydrate the dry hydratable compound, 35 thereby generating heat which helps the agglomeration process to continue. Moreover, the hydration of the hydratable compound is believed to lead to solid bridging which further improves the structure of the granules. (Thus, the addition of the water to the hydratable compound before the latter is added to the spray-dried material, though not precluded, is not favoured, since it may lead to premature hydration of the hydratable compound.) Furthermore, the water improves the binding ability of any nonionic surfactant that 40 may be present by making it very sticky; this helps to form strong agglomerates.

The spray-dried material obtained from the spray-drying tower may typically have a particle size in the range from 350 to 550 µm. After the first (usually high-speed or high-shear) mixing step or phase, the average particle size will generally be reduced, typically to a value of about 300 µm. On account of the agglomeration step or phase in the second mixer, the average particle size will typically be increased to a 45 value of from 500 to 800 µm. The increase in particle size and a reduction in fines (particles less than 250µm in size) are believed to be important factors in the dispensing improvements that can be achieved by means of this invention. In general, the product obtained by the present process should have a content of fines (< 250µm) of less than 10%, preferably less than 5%, by weight.

One or more further components may be added to the mixture between the first and second mixers 50 and/or in the second mixer. For example, it may be advantageous to add further hydratable compound, preferably anhydrous sodium carbonate, to the mixture in the second mixer. It is also possible to add a fine powder, such as silica, calcium carbonate, talc or, preferably, aluminosilicate, e.g. zeolite, although it is preferred that the addition of this material be made, if at all, not earlier than half-way along, more preferably at least two-thirds of the way along, and most preferably at or near the end of, the second mixer or after 55 agglomeration is substantially complete, so as to avoid or at least reduce any adverse effect on the agglomeration process. Such fine powders will typically have an average particle size of from 0.01 to 100µm, preferably from 0.1 to 10µm.

Yet another procedure involves deferring the addition of the hydratable compound until after the treatment of the spray-dried material in the first (usually high-speed) mixer; thus, it is possible to add the hydratable compound in the second mixer. In such cases, the water may be added in the second mixer and/or beforehand, e.g. in the first mixer. Portionwise addition of the hydratable compound at different stages of the present process is also possible.

5 A modification of the above-described two-step mixing (dual mixer) embodiments is to dispense with one of the mixers. Thus, the mixing of the hydratable compound and water with the spray-dried material can also be accomplished in a single mixer but sufficient energy should be supplied by the mixer to distribute and mix the hydratable compound and the water well with the spray-dried material in a single-step 10 operation. Sufficient energy should also be imparted to the material to consolidate it into a denser form while it is in a deformable state. For these reasons it is preferred to employ a high-speed mixer; however, a moderate speed mixer can be used, although this will take longer.

15 Use may also be made of a variable speed batch mixer, such as the Eirich R09 mixer, by treating the material therein under high-speed conditions in a first step and then under moderate-speed conditions in a second step. The first and second steps in such an embodiment may be analogous to the first and second mixing steps in the dual mixer embodiments.

20 The agglomerated, or granular, material obtained after the treatment in the mixer(s) and the addition (if any) of water may be subjected to drying and/or forced cooling, for example in one or more fluidised-bed apparatuses. The fluidised-bed treatment may also be carried out for the purpose of ageing the agglomerates or granules in order to accelerate hydration therein.

The agglomerated or granular material may, if appropriate after drying and/or cooling, have one or more further components admixed thereto in order to prepare a finished detergent powder product. Thus, for example, further liquid material, such as perfume, liquid suds-suppressor or nonionic surfactant, can be sprayed on in a mix drum.

25 The granular material obtained by the process of the present invention generally contains little or no fines and therefore contributes to the aesthetics of the finished product, which will not appear dusty. Moreover, the detergent granules so obtained have been found to have excellent dispensing and solubility characteristics and to have a reduced tendency to cake upon storage.

30 The present invention is illustrated in and by the following examples, in which parts and percentages are by weight unless otherwise stated

#### Example 1

Spray-dried detergent powders were made according to the following composition:

35

	Composition (Parts)	
	a	b
40	Linear Alkyl Benzene Sulfonate	15.2
	Zeolite A	24.0
	Polyacrylate Polymer	5.0
	Chelating Agent	0.3
	Carboxy Methyl Cellulose	0.4
	Fluorescent Brightener	0.1
45	Sodium Carbonate	15.0
	Moisture	4.0
		3.0

50 The detergent powder (a) was mixed with 5 parts of nonionic surfactant in a high shear mixer, a Lödige CB30. This product was then passed to a second, moderate speed mixer, a Lödige KM600, wherein it was mixed with 4 parts of zeolite A which were fed into the front end of the mixer.

The detergent powder (b) was mixed with 5 parts of nonionic surfactant in a high shear mixer, a Lödige CB30. The product was passed to a second, moderate-speed mixer, a Lödige KM600, wherein it was mixed with 10 parts anhydrous sodium carbonate. 5 parts of water were added by spraying the water through a pressure nozzle. 4 parts of zeolite A were added at the rear end of the second mixer.

55 The following operating conditions for the mixers were employed in the processing of both powders: the Lödige CB30 was operated with a shaft speed of 2000 r.p.m., the material therein having a residence time of 20 seconds and attaining a temperature of 20 °C, whereas the Lödige KM600 was operated at 200 r.p.m..

EP 0 643 129 A1

the material therein having a residence time of 4 minutes and attaining a temperature of 45°C.

The resulting detergent granules were dried for 2 minutes at 80°C in a fluidized bed to a moisture content of 4 parts. The material was then cooled down to 20°C in a fluidised bed over a period of 2 minutes. The average particle size of the resultant product (a) was 300µm, whereas the average particle size of the resultant product (b) was 600µm.

5 The products from both tests were each mixed with other detergent components in a rotating drum according to the following compositions (parts):

	Product	A	B
10	Detergent Granules (a)	70	-
	Detergent Granules (b)	-	70
	Sodium Perborate Monohydrate	16	16
	TAED	5	5
15	Sodium Silicate 2R	5	5
	Protease Enzyme	1	1
	Lipase Enzyme	0.2	0.2
	Perfume	0.3	0.3
	Suds Suppressor	0.5	0.5
20	Nonionic Surfactant C <sub>25</sub> AE <sub>3</sub>	1.0	1.0

The products had identical compositions, but product (A), which had a bulk density of 820g/l, had an average particle size of 350µm (with a fines content (< 250 µm) of about 20% by weight), whereas product (B), which had a bulk density 820g/l, had an average particle size of 580 µm (with a fines content (< 250 µm) of below 5% by weight).

25 The two products were tested in a washing machine dispenser using the following procedure. 100g of each product were placed in the drawer of a washing machine dispenser and water was added at 2 litre/min for 2 minutes. At the end of each test the washing machine drawer dispenser was removed and the amount of residue weighed. The residual material was expressed as a percentage of the original dry matter.

30 The following result was obtained:

	Machine\Product	Residue (%)	
		A	B
35	Zanussi (trade name)	90	5

40 Example 2

A spray dried detergent powder was produced according to the following composition:

		Parts
45	Linear Alkyl Benzene Sulfonate	18
	Alkyl Polyglucoside	3
	Sodium Tripolyphosphate	20
	Sodium Silicate 1.6 R	8
50	Sodium Polyacrylate Polymer	6
	Chelating Agent	0.2
	Moisture	4

55 The spray-dried powder was mixed with 10 parts of anhydrous sodium tripolyphosphate in a variable speed Eirich RO9 mixer for 10 seconds; in this step the mixer was operated with a speed of 1000 r.p.m., the material therein attaining a temperature of 40°C. 5 parts of water were added to the mixer and mixed for 30 seconds; in this step the mixer was operated with a speed of 200 r.p.m., the material therein attaining a temperature of 55°C. The product (densified detergent granules) was then removed and mixed in a

EP 0 643 129 A1

rotating drum with other detergent ingredients to form a finished product of the following composition:

	Parts
5	Densified Detergent Granules                    74
	Sodium Bicarbonate                              10
	Sodium Citrate Dihydrate                      10.8
	Savinase™ Enzyme                                1.0
	Cellulase Enzyme                                0.2
10	Lipase Enzyme                                    0.4
	Perfume    0.4
	Polyvinyl Pyrrolidone                          0.5
	Nonionic Surfactant                            2.0
	Suds Supressing Agent                          0.5

15

The average particle size of the product, which had a bulk density 780g/l, was 500 µm (with a fines content (< 250µm) of below 5% by weight). 100g of the product were placed in the dispensing drawer of a washing machine. Water was added at 2 litre/min for 2 minutes at 20 °C and the following results were obtained:

20

Machine	Residue (%)
Zanussi (trade name)	0

25

Example 3

30

A spray-dried detergent powder was produced according to the following composition:

35

	Parts
	Tallow Alcohol Sulfate                        3
	Linear Alkyl Benzene Sulfonate            12
35	Zeolite A                                        26
	Sodium Carbonate                              5
	Fluorescent Brightener                        0.1
	Moisture                                        4

40

The spray-dried powder was added into a continuous Lödige CB40 mixer, into which 5 parts of sodium bicarbonate, 5 parts of anhydrous citrate and 6 parts of polyacrylate polymer solution (40%) were also added. The Lödige CB40 was operated at 1000 r.p.m., the material therein having a residence time of 30 seconds and attaining a temperature of 30 °C. The resulting mixture was passed to a second mixer, a Lödige KM4200, where it was allowed to agglomerate. The Lödige KM400 was operated at 80 r.p.m., the material therein having a residence time of 3 minutes and attaining a temperature of 50 °C. The product leaving the Lödige KM4200 mixer was passed to a fluidized bed drier, where it was dried for 2 minutes at 80 °C to a moisture content of 4 parts. The material was then cooled down to 20 °C in a fluidised bed over a period of 2 minutes. The product (densified detergent granules) was then mixed with other ingredients in a rotating drum to form a finished product according to the following composition:

45

50

The spray-dried powder was added into a continuous Lödige CB40 mixer, into which 5 parts of sodium bicarbonate, 5 parts of anhydrous citrate and 6 parts of polyacrylate polymer solution (40%) were also added. The Lödige CB40 was operated at 1000 r.p.m., the material therein having a residence time of 30 seconds and attaining a temperature of 30 °C. The resulting mixture was passed to a second mixer, a Lödige KM4200, where it was allowed to agglomerate. The Lödige KM400 was operated at 80 r.p.m., the material therein having a residence time of 3 minutes and attaining a temperature of 50 °C. The product leaving the Lödige KM4200 mixer was passed to a fluidized bed drier, where it was dried for 2 minutes at 80 °C to a moisture content of 4 parts. The material was then cooled down to 20 °C in a fluidised bed over a period of 2 minutes. The product (densified detergent granules) was then mixed with other ingredients in a rotating drum to form a finished product according to the following composition:

55

EP 0 643 129 A1

	Parts
5	Densified Detergent Granules                    60.1
	Sodium Percarbonate                            15.0
	Layered Silicate Granules                    10.0
	Bleach Activator, TAED                    5.0
	Protease Enzyme                                1.4
	Suds Suppressor Granules                    1.5
	Alcohol Ethoxylate C <sub>25</sub> E <sub>3</sub> 5
10	Perfume                                        0.5
	Soil Release Polymer                        0.3
	Detergent Speckle                            1.0
	Lipase Enzyme                                0.2

15      The average particle size of the product, which had a bulk density 850g/l, was 640 µm (with a fines content (< 250 µm) of below 5% by weight). The product was tested in a washing machine dispenser at 2 litres/min for 2 minutes at 20 °C, and the following result was obtained:

20	Machine	Residue (%)
	Zanussi	2

25      Dispensing benefits comparable to those noted in Examples 1, 2 and 3 were observed when using washing machines supplied by other washing-machine manufacturers.

Example 4

30      A spray-dried detergent powder was made according to the following composition (parts):

35	Linear Alkyl Benzene Sulfonate                    8.40
	Polymer    3.90
	Sodium Sulfate                                    12.83
	Sodium Silicate                                    2.6
	Chelating Agent                                    0.4
	Zeolite    9.7
40	Fluorescent Brightener                            0.17
	Nonionic Surfactant                            9.0
	Moisture    6.0

45      The spray-dried powder was mixed with 10 parts of sodium carbonate in a high-speed mixer, a Lödige CB30. The product was then passed to a second, moderate speed mixer, a Lödige KM600 where 2 parts of water were added by spraying the water through a pressure nozzle.

The following operating conditions were employed in the processing of the powder. The Lödige CB30 was operated at a shaft speed of 1500 rpm, the material therein having a residence time of 25 seconds, and attaining a temperature of 25 °C. The Lödige KM600 was operated at 200 rpm, the material therein having a residence time of 5 minutes and attaining a temperature of 50 °C.

50      The resulting detergent granules were dried for 2 minutes at 80 °C in a fluidised bed to a moisture content of 4 parts. The material was then cooled down to 20 °C in a fluidised bed for 2 minutes. The average particle size was 650µm.

The product was mixed with other detergent components in a rotating drum according to the following composition (parts):

55

5	Detergent granules	61.0
	Soap flakes	3.00
	Coconut alkyl sulphate extrudates	6.80
	Suds suppressor particles	0.50
	Perborate monohydrate	18.0
	TAED	7.00
	Protease Enzyme	0.30
10	Savinase Enzyme	3.00
	Perfume	0.40

The finished product had a bulk density of 800g/l and an average particle size of 600µm (with a content of fines (< 250µm) of below 5% by weight).

It will of course be understood that the present invention has been described above purely by way of example and that modifications of detail can be made within the scope of the invention.

#### Claims

1. A process for preparing a granular detergent composition or component having a bulk density of at least 650g/l, which process comprises treating a spray-dried material in a mixer, characterised in that water is added to and/or included in the spray-dried material, and in that the spray-dried material is treated in the mixer in the presence of a hydratable compound.
2. A process according to claim 1, characterised in that the spray-dried material is treated in the said mixer also in the presence of water, being water added to and/or present in the spray-dried material.
3. A process according to claim 1 or 2, characterised in that the hydratable compound is a hydratable salt, e.g. sodium carbonate.
4. A process according to claim 1, 2 or 3, characterised in that the hydratable compound is added in an amount of up to 35% by weight of the dry matter in the spray-dried material.
5. A process according to any of claims 1 to 4, characterised in that the total of water added to and present in the spray-dried material is up to 30%, preferably up to 25%, by weight of the dry matter in the spray-dried material.
6. A process according to any of claims 1 to 5, characterised in that water is added to the spray-dried material in an amount of from 0 to 20%, preferably 0 to 15%, by weight of water relative to the dry matter in the spray-dried material.
7. A process according to any of claims 1 to 6, characterised in that the spray-dried material is treated in the mixer in the presence of a nonionic surfactant, the latter preferably being present in an amount of up to 15% by weight of the dry matter in the spray-dried material.
8. A process according to any of claims 1 to 7, characterised in that the spray-dried material is treated in a first, preferably high-speed, mixer and is subsequently treated in a second, preferably moderate-speed, mixer.
9. A process according to claim 8, characterised in that the first mixer comprises a mixing chamber containing a rotatable shaft on which are mounted a plurality of mixing elements, the shaft in operation rotating at a speed of from 100 to 2500 rpm.
10. A process according to claim 8 or 9, characterised in that the second mixer comprises a mixing chamber containing a rotatable shaft on which are mounted a plurality of mixing elements, the shaft in operation rotating at a speed of from 40 to 160 rpm.
11. A process according to claim 8, 9 or 10, characterised in that the spray-dried material is mixed with hydratable compound in the first mixer and water is added to the resultant mixture in the second mixer.

**EP 0 643 129 A1**

12. A process according to claim 8, 9 or 10, characterised in that hydratable compound and water are both added to the spray-dried material in the first mixer.
- 5      13. A process according to claim 8, 9 or 10, characterised in that hydratable compound and water are both added to the spray-dried material in the second mixer.
14. A process according to any of claims 1 to 7, characterised in that the spray-dried material is treated in a single mixer in which it is mixed with hydratable compound and water.
- 10     15. A process according to claim 14, characterised in that the mixer is a variable-speed machine and the spray-dried material is treated therein in two steps, the machine being operated at higher speed in the first step than in the second step.
- 15     16. A process according to any of claims 1 to 15, characterised in that the average particle size of the spray-dried material is increased in the said mixer or the said second mixer, as the case may be, preferably to a value of from 500 to 800  $\mu\text{m}$ .
- 20     17. A process according to any of claims 1 to 16 characterised in that the material obtained after treatment in the said mixer or second mixer, as the case may be, is subjected to drying and/or cooling, preferably in at least one fluidised bed.
18. A product of a process according to any of claims 1 to 17, characterised in that its content of particles having a particle size of less than 250  $\mu\text{m}$  is less than 10%, preferably less than 5%, by weight.

25

30

35

40

45

50

55



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 20 2607

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
X	EP-A-0 351 937 (UNILEVER) * page 4, line 30 - page 5, line 21; claims 1-11; examples 1,6-8 *	1-6, 8-10,16	C11D17/06 C11D11/00						
D,X	EP-A-0 367 339 (UNILEVER) * claims; examples *	1-6,8-18							
A	FR-A-2 277 147 (HENKEL) * claim 1 *	1,7							
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-021916 & JP-A-4 348 198 (LION CORP.) 27 May 1991 * abstract *	1-6							
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)						
			C11D						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>28 January 1994</td> <td>Grittern, A</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	28 January 1994	Grittern, A
Place of search	Date of completion of the search	Examiner							
THE HAGUE	28 January 1994	Grittern, A							
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons M : member of the same patent family, corresponding document							